

# *Electrolyte Reactivity and Its Implication for Solid-Electrolyte Interface (SEI) Formation*

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**Also showing work from SEista collaborator groups of Nanda, Neale and Toney**

**Project ID bat344**

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# Overview

## Timeline

- October 1<sup>st</sup> 2016 - September 30<sup>st</sup> 2019.
- Percent complete: 40%

## Budget

- Funding for FY 18: \$3900K

Support for the electrolyte and interface work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Brian Cunningham and David Howell, and Tien Duong for solid electrode bulk work

## Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

## Partners

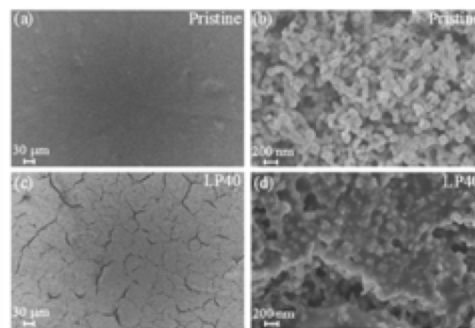
- The SEISta Team led by NREL
  - Sandia National Laboratory
  - Argonne National Laboratory
  - Oak Ridge National Laboratory
  - Lawrence Berkeley National Laboratory
- UC Berkeley
- Colorado University Boulder
- Colorado School of Mines
- University of Rhode Island

# Milestones

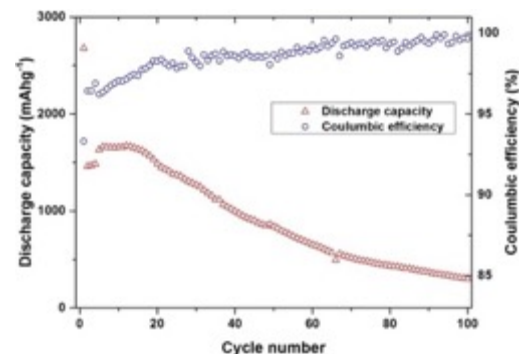
Month Year	Milestone	Status
October 2017	Have completed the selection and characterization (XPS, SIMS, IR, and Raman), including determination of the surface termination chemistry and impurity levels, of the SEISta model research samples to be used by all members of the team in FY18.	<b>100% complete</b>
January 2018	Have characterized (XPS, SIMS, IR, and Raman) the surface chemistry and composition of the SEISta model research samples after contact with the electrolyte, before cycling, including the nature of the electrolyte decomposition products.	<b>100% complete</b>
April 2018	Completed characterization (electrochemistry, IR and Raman) of the early stage silicon electrolyte interphase formation on the SEISta model research samples, specifically by establishing and demonstrating a procedure for quantitatively measuring the solubility of SEI on silicon surfaces.	ongoing
July 2018	Established and demonstrated a procedure for measuring the growth rate of silicon SEI components at fixed potentials and during cycling. Have determined how the physical properties of the silicon electrolyte interface are influenced by the nature of the silicon surface on the SEISta model samples.	ongoing

# Relevance

- Si anodes exhibit desirable high capacity combined with fade and poor shelf life
- SEI formation in Si, as function of electrolyte formulation, cycling and Si surface composition, not well understood



SEM images recorded with two different magnifications of the surface morphologies of pristine silicon electrodes (a,b) and after 85 cycles in the LiPF<sub>6</sub> EC/DEC electrolyte



Discharge capacity and Coulombic efficiency versus cycle number for the Si electrode

*Chem. Mater.* **2015**, 27, 2591–2599

*Electrochimica Acta* **2017**, 253 85–92

## Objectives:

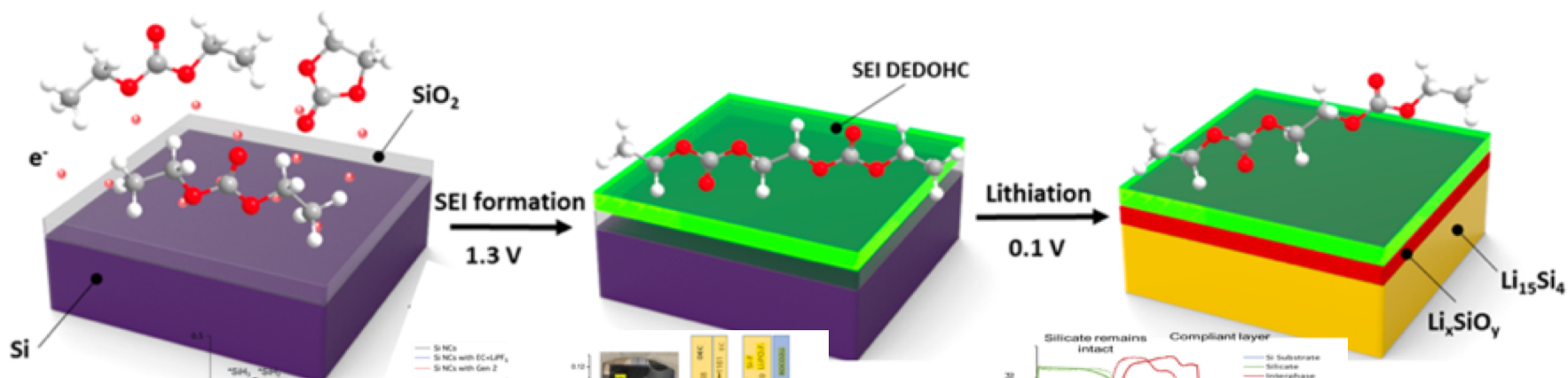
- Understanding the bulk and interface speciation in Si electrolytes as it relates to chemical degradation
- Understanding the impact of the native surface SiO<sub>2</sub> in the passivation of the Si electrode, Li diffusion and reactivity with the electrolyte.

## Relevance:

- To use the derived bottoms-up understanding to suggest improved cycle-life electrolyte and electrode formulations.

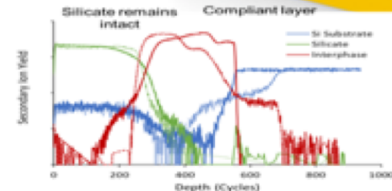
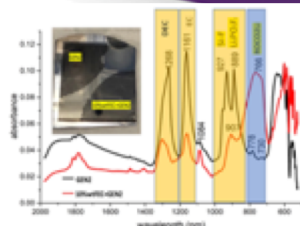
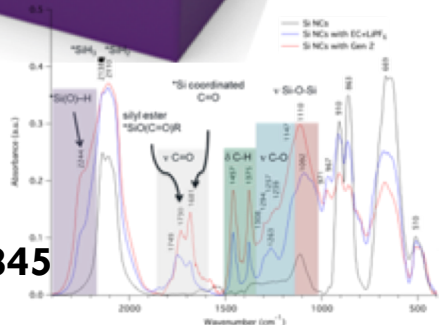


# Chemical reactivity vs electrochemical reactivity



# Chemical Reactivity of Silicon

## Project ID BAT345



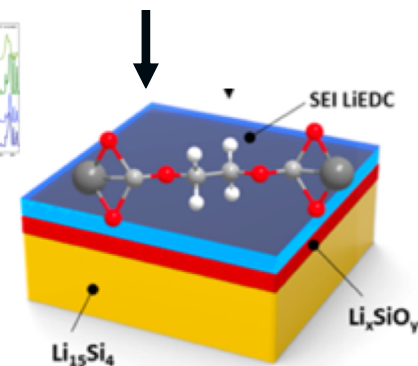
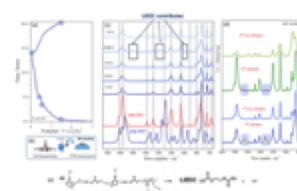
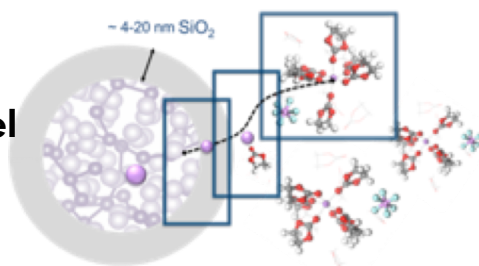
## Surface analysis of the Silicon SEI

## Role of Li Silicates in Si SEI Formation ID BAT348

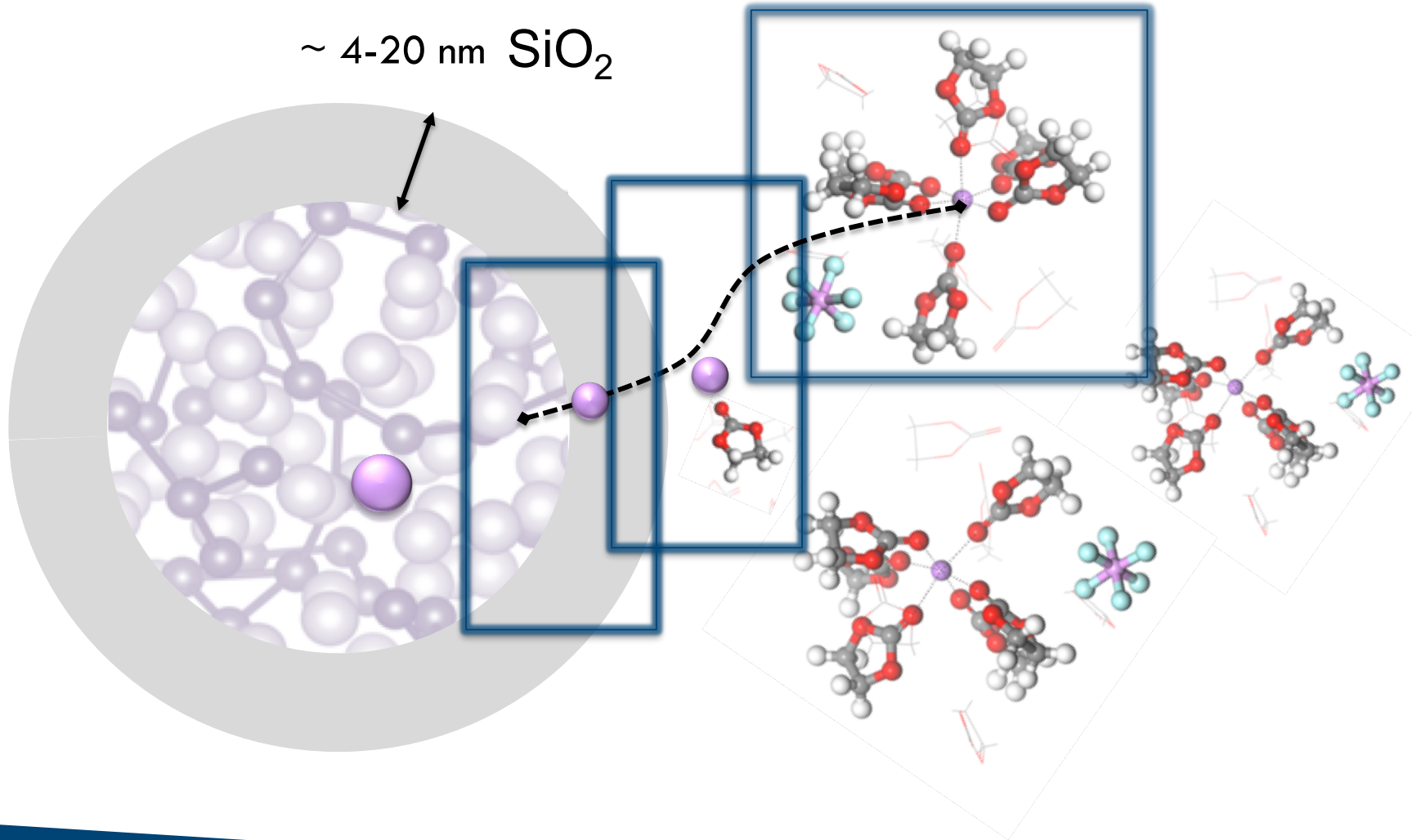
## Spectroelectrochemistry on silicon ID BAT364

# Predicting and Understanding Novel Electrode Materials From First-Principles

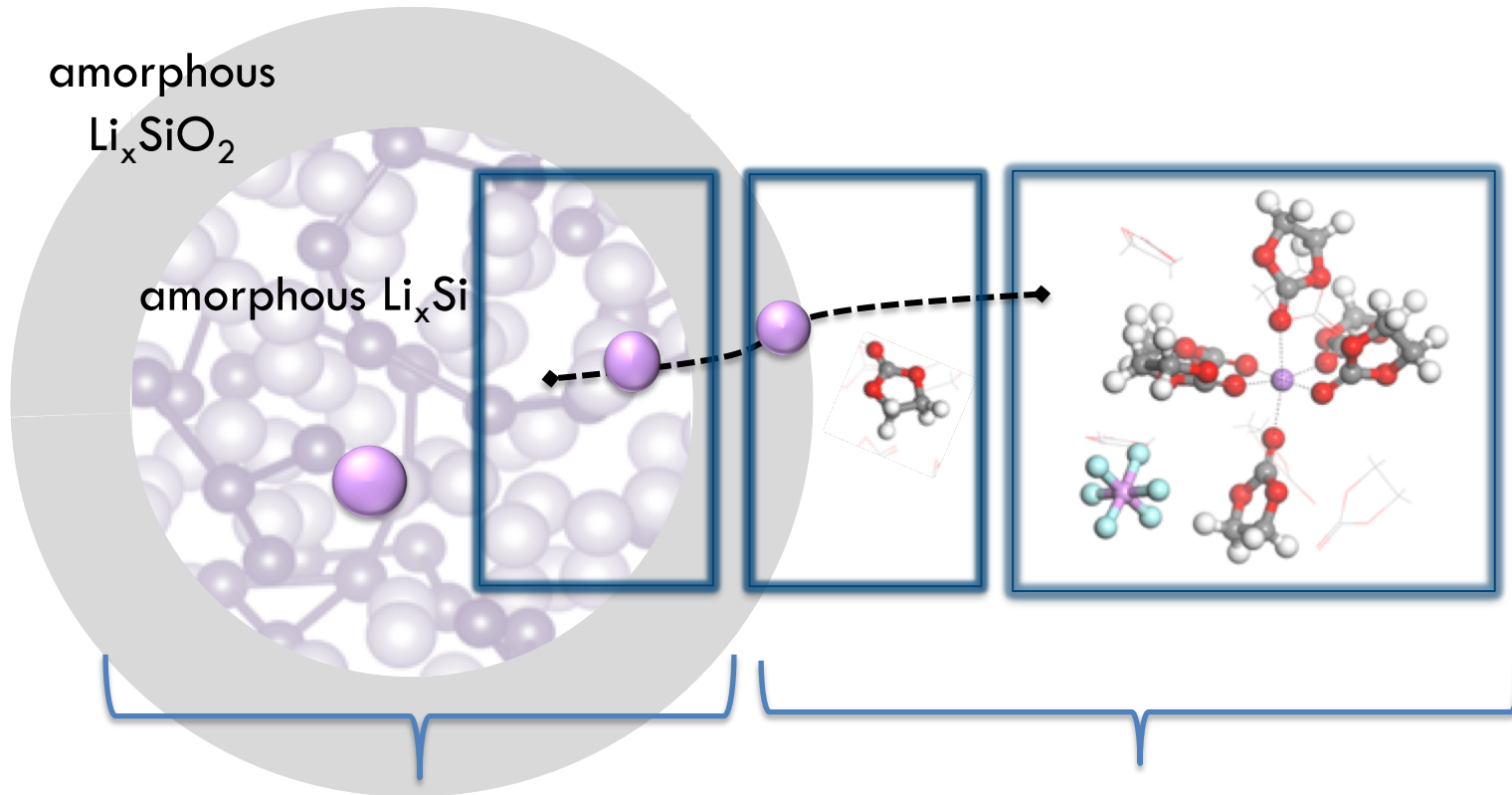
Project ID BAT344



# Approach: From Bulk Electrolyte to Bulk Electrode



# Approach: From Bulk Electrolyte to Bulk Electrode



**Ab initio molecular dynamics** for formation of amorphous Li-Si-O structures, voltage profiles, and Li diffusion

**Ab initio calculations** for reactivity between electrolyte components and  
**Classical molecular dynamics** for bulk and interfacial solvation structures and desolvation process at interface

# Approach: MD and First-principles parameters

Bulk electrolyte: 1.0 M  $\text{LiPF}_6$  in pure EC and 5-10% FEC classical molecular dynamics

Force field form	EC	Li	$\text{PF}_6$
OPLS	OPLS-AA charge recalculated	Refined OPLS	OPLS-AA

- 1500 EC, 75-150 FEC + 104  $\text{LiPF}_6$  molecules
- $T = 298 \text{ K}$
- Equilibrated at 1 atm, 5 ns NVT

$\text{SiO}_2$ - electrolyte interface classical molecular dynamics

Force field form	$\text{LiPF}_6/\text{EC}$	$\text{SiO}_2/\text{Crystalline Si}$
OPLS	OPLS-AA as above	Tersoff (electrode) ClayFF (electrode-electrolyte)

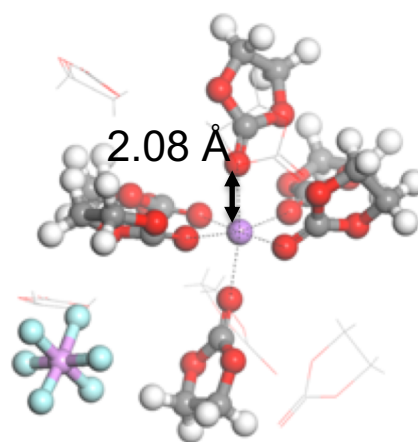
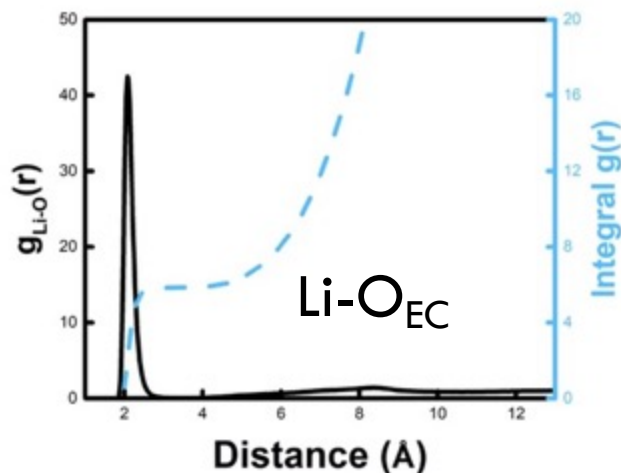
- Fixed charge (fixed potential coming)
- 1300 EC, 100  $\text{LiPF}_6$  molecules
- $T = 400 \text{ K}$ ;  $(54.69 \times 54.69) \times 50 \text{ \AA}$  where 50  $\text{\AA}$  is the distance btw  $\text{SiO}_2$  layers
- Box size determined at 1 atm
- $> 2 \text{ ns NVT}$

First principles molecular dynamics and IR spectra

Functional	ENCUT	Functional and basis set
GGA+U	400	B3LYP/6-31+g*

# Results: Bulk Electrolyte Speciation 1 M LiPF<sub>6</sub> in EC

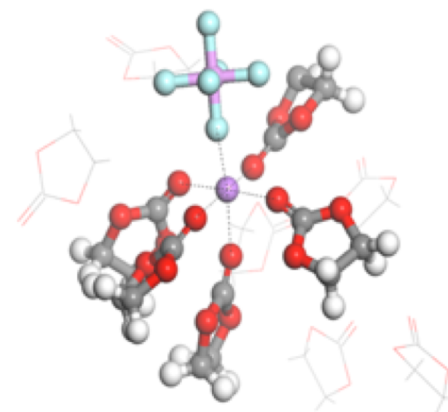
1 M LiPF<sub>6</sub> in EC



**Majority species**

~ 94% SSIP\*

Li coordinated with ~5.8 EC



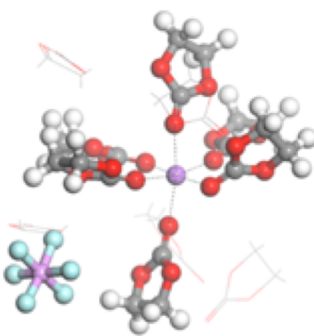
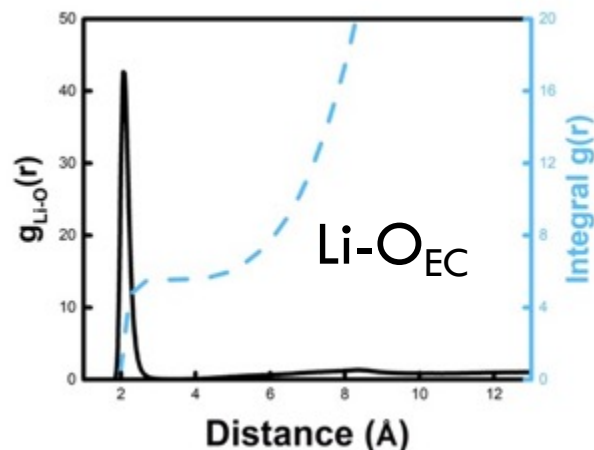
**Minority species**

~6 % CIP\* Li coordination with  
4-5 EC and 1 PF<sub>6</sub><sup>-</sup>

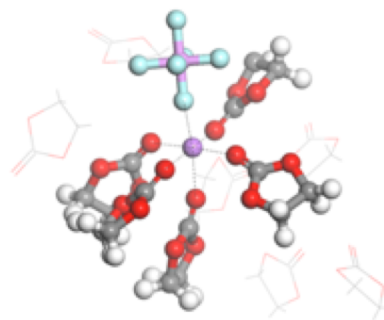
- In 1 M LiPF<sub>6</sub>/EC at 298 K the majority species are solvent-separated ion-pairs; however about 6% contact ion-pairs are also found, which will impact reduction potential of PF<sub>6</sub>

# Results: Bulk Electrolyte Speciation 1 M $\text{LiPF}_6$ in EC + 5% FEC

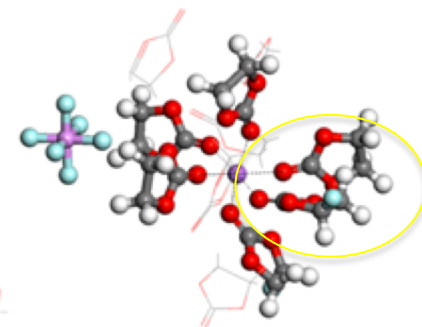
1 M  $\text{LiPF}_6$  in EC + 5% FEC



**Majority species**  
~ 79% SSIP\*  
Li coordinated ~5.5 EC



~9 % CIP

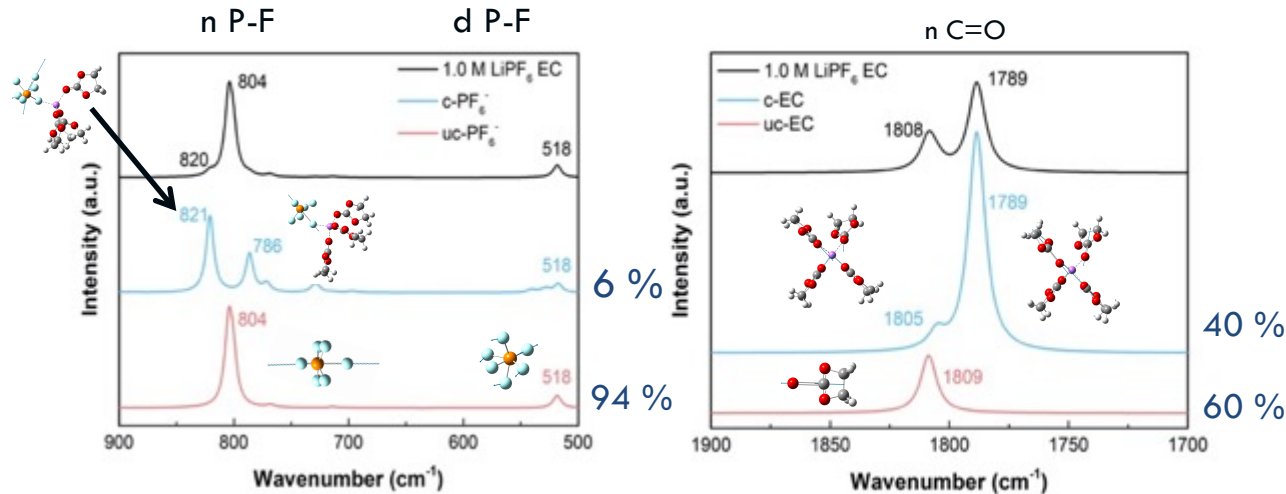
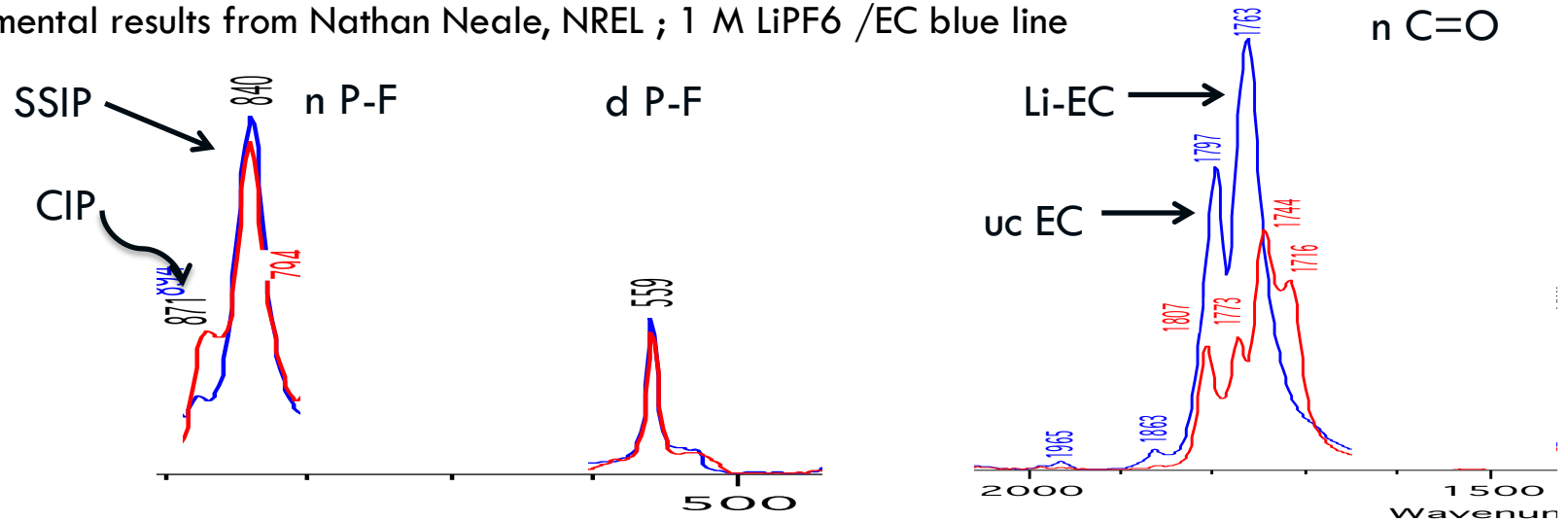


**Minority species**  
~12 % FEC-  
coordinated SSIP

- Adding FEC decreases the solvation strength of the combined solvent, reduces the solvent coordination with Li, causes increase in contact ion pairs, and ~12% SSIPs with 1 FEC.

# Results: Verifying Bulk Electrolyte Speciation

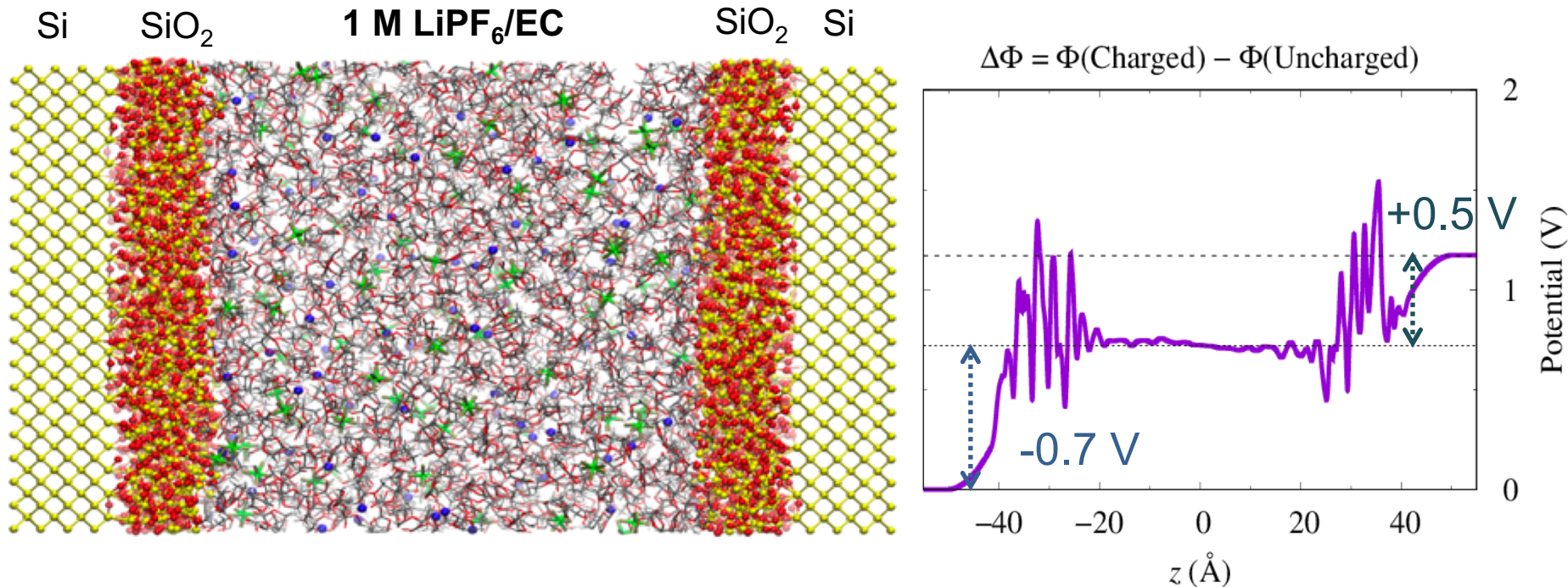
- Experimental results from Nathan Neale, NREL ; 1 M LiPF<sub>6</sub> /EC blue line



While the absolute IR spectra are shifted between experiment and calculations, the relative shift between CIP vs SSIP are in agreement and shows that the calculated speciation is consistent with experimental trends.



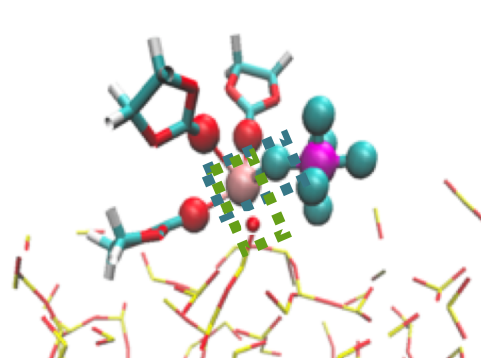
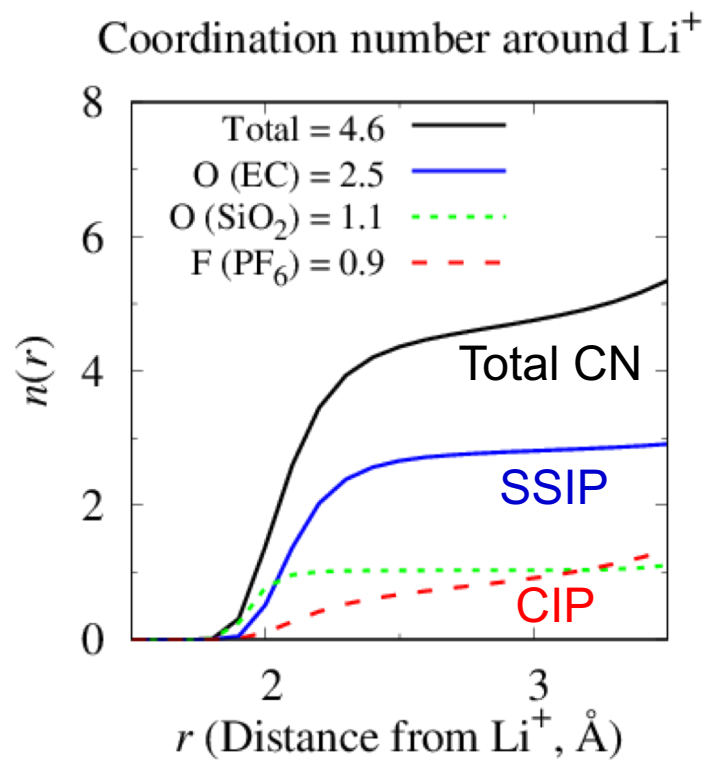
# Results: Interface simulations with Constant Charge



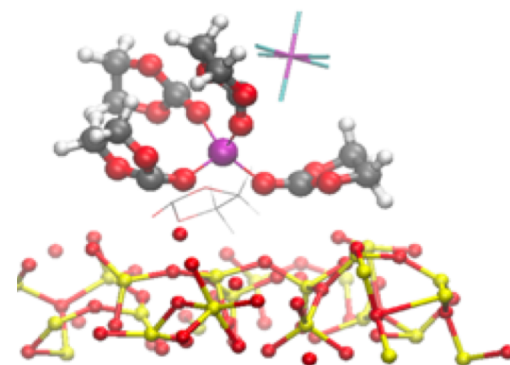
- Symmetric Si/SiO<sub>2</sub>/LiPF<sub>6</sub> in EC cell using constant charge model
- Varying +/-e is uniformly assigned to 1600 Si atoms in positive/negative electrodes, respectively
- Potential profile shows plateau in bulk region,  $|z| < 20$  Å. => well equilibrated



# Results: Interface promotes CIP and Reduced EC coordination



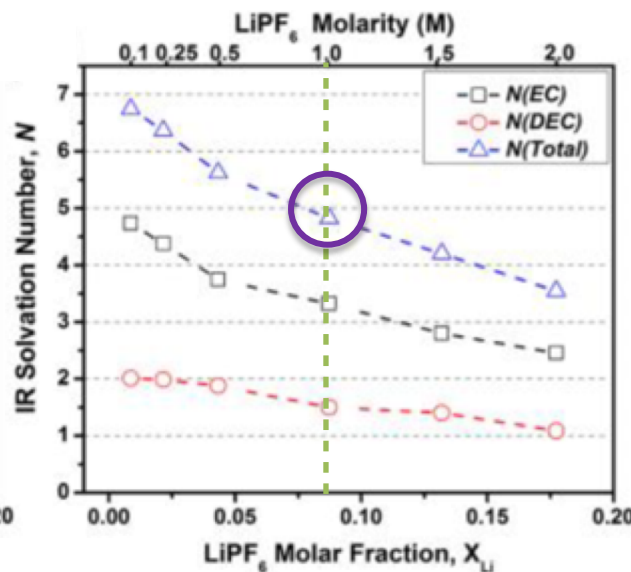
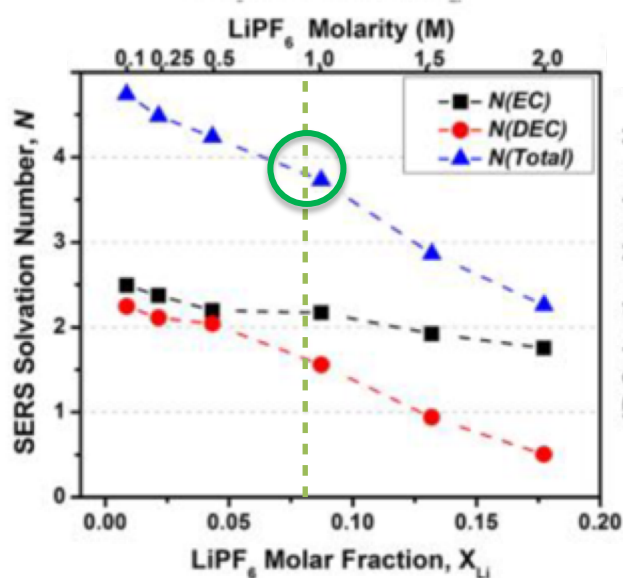
**Majority species (400K)**  
~ 65% CIPs\*  
Li coordinated ~2-3 EC



**Minority species (400 K)**  
~35 % SSIPs\*

- Interface is defined as the region within 4 Å from the  $\text{SiO}_2$  surface
- The significant interaction between oxygen at the  $\text{SiO}_2$  interface and  $\text{Li}^+$  reduces the CN of EC.
- CIPs population is doubled at the interface as compared to the bulk electrolyte (30% at 400K)
- Higher temperature favors the formation of CIPs as compared to SSIPs, in both bulk and interface.
- Total solvation number =  $\text{CN}(\text{EC}) + \text{CN}(\text{PF}_6) + \text{CN}(\text{SiO}_2) = 4.6$

# Results: Comparison to experimental bulk electrolyte speciation

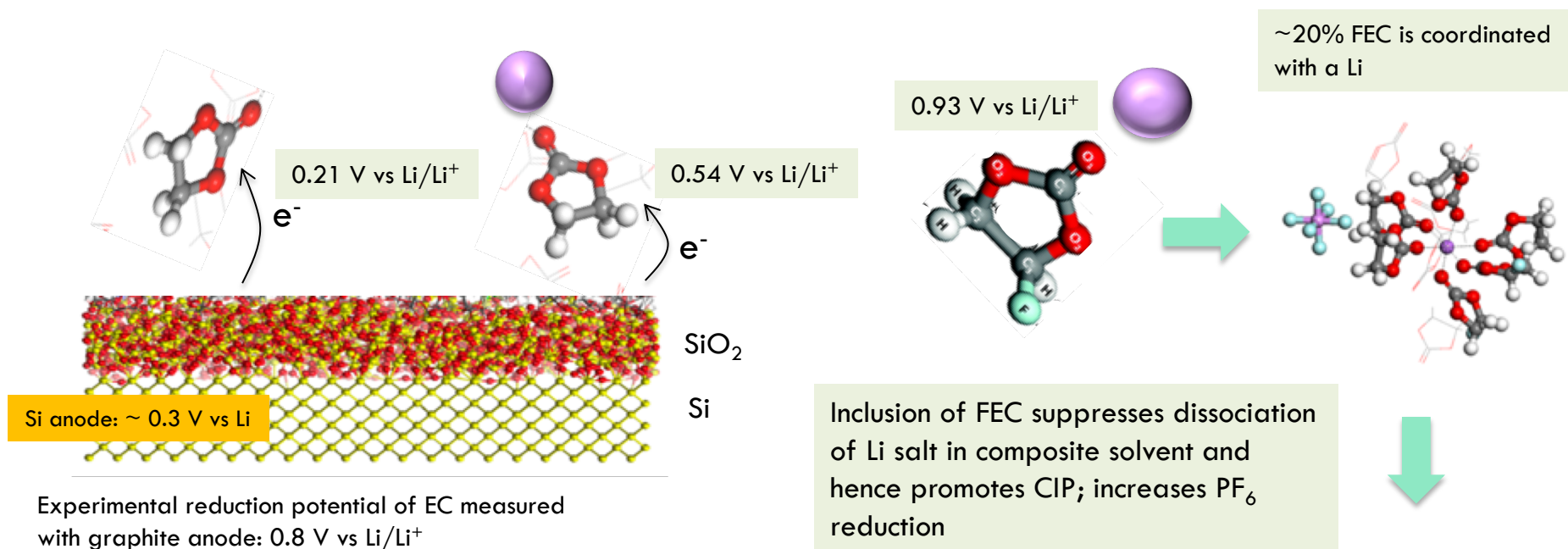


$\text{LiPF}_6$  in EC:DEC (1:1 vol) with Au nano particle (NP) at 300 K

G. Yang, I. N. Ivanov, R. E. Ruther, R. L. Sacci, V. Subjakova, D. T. Hallinan, J. Nanda, *ACS Nano* (submitted)

- IR measurements of solvation number for 1 M  $\text{LiPF}_6$  are in agreement with our calculated CN of EC in bulk: **5** and **5.5**, respectively.
- However, SERS CN of EC/DEC differs from ours at the interface: 3.7 and 2.5, respectively. Unlike the Au NP, we expect significant interaction between oxygen at the  $\text{SiO}_2$  interface and  $\text{Li}^+$  which reduces the interfacial EC coordination with Li.

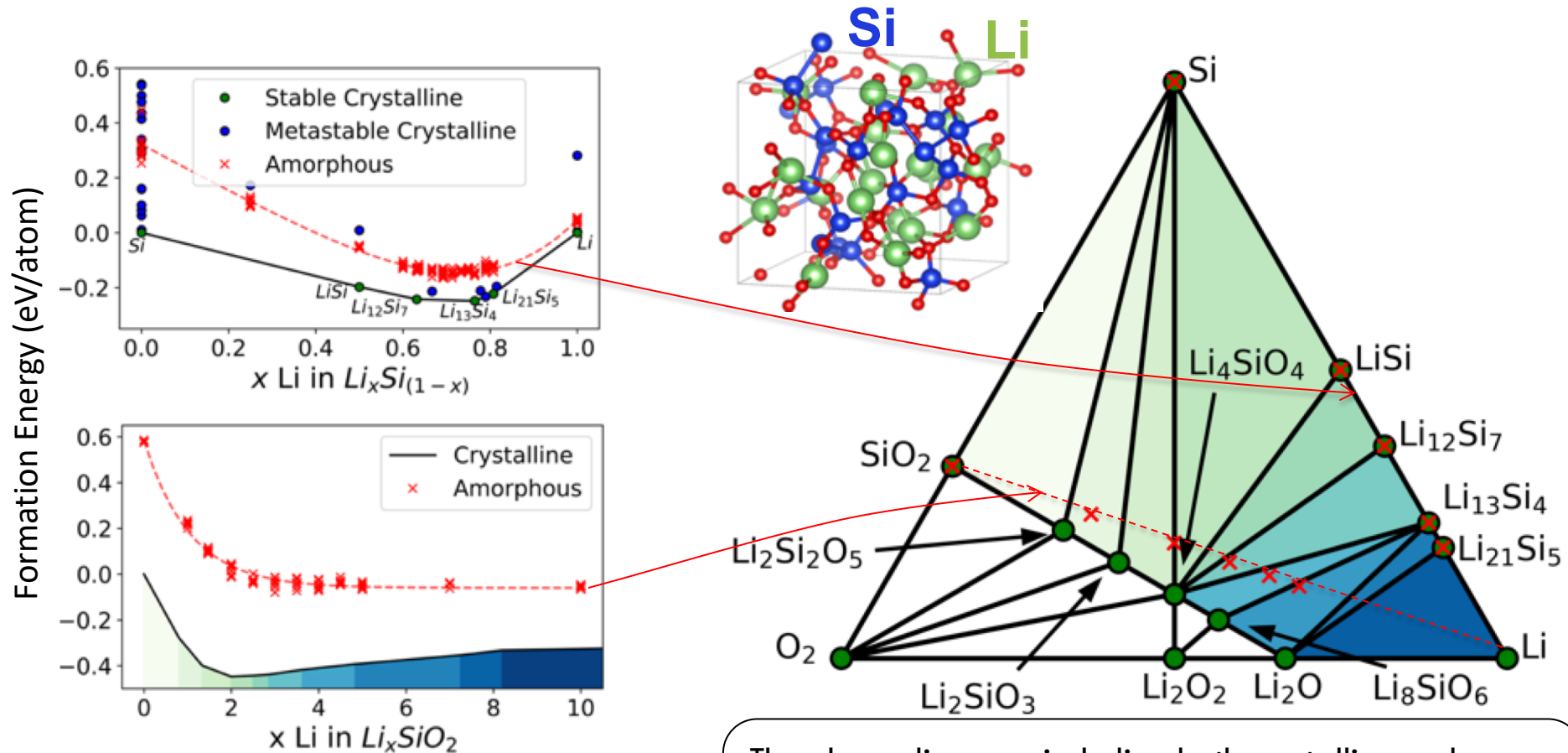
# Results: Speciation Impact on Reduction Potentials



Majority and interface speciation influences what molecules reduce as a function of voltage

- Coordination with Li<sup>+</sup> increases reduction potential of solvent and anion
- FEC increases CIP which in turn increases PF<sub>6</sub> reduction
- 20% of FEC is coordinated with Li<sup>+</sup>, increasing its reduction potential

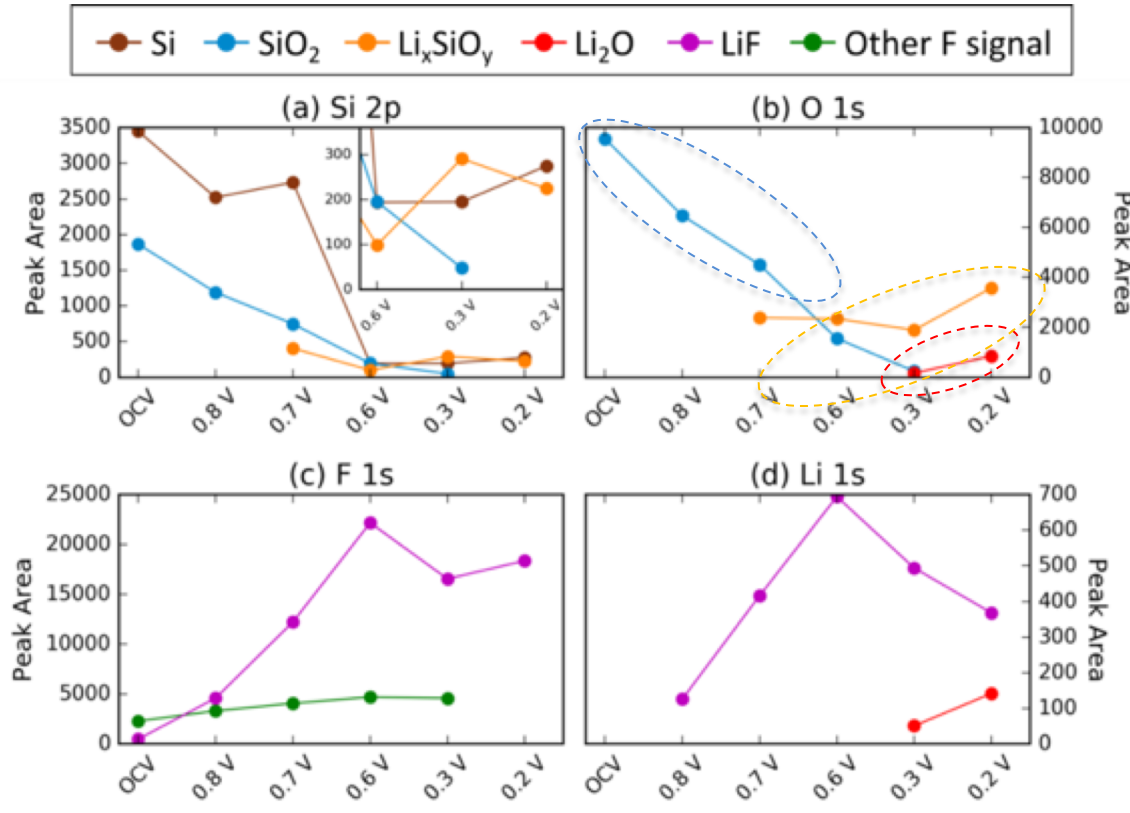
# Results: Phase diagram (Si-Li-O) including amorphous phases



The phase diagram, including both crystalline and amorphous phases, predicts  $SiO_2$  to lithiate, and form increasing Li-O and Li-Si bonds, at the expense of Si-O environments.

# Results: XAS of Si wafer supports

## Lithiation of SiO<sub>2</sub>

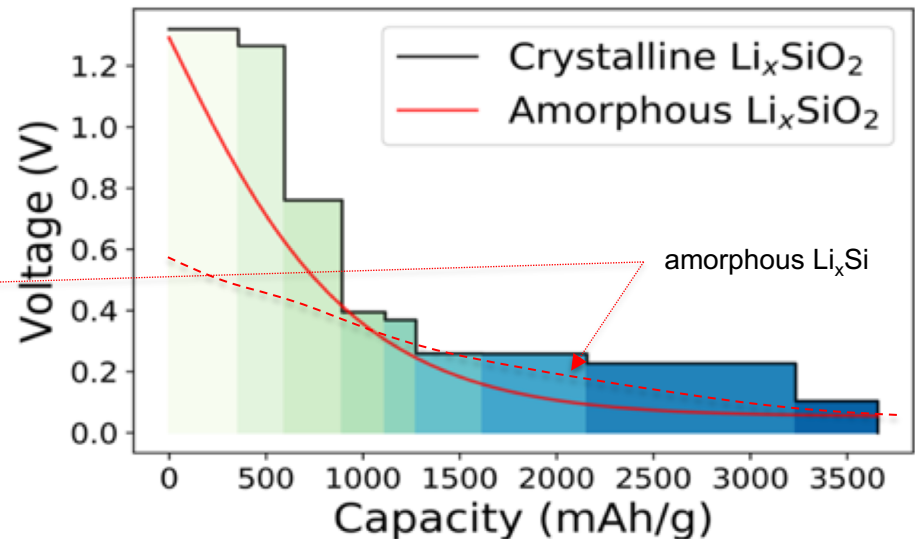
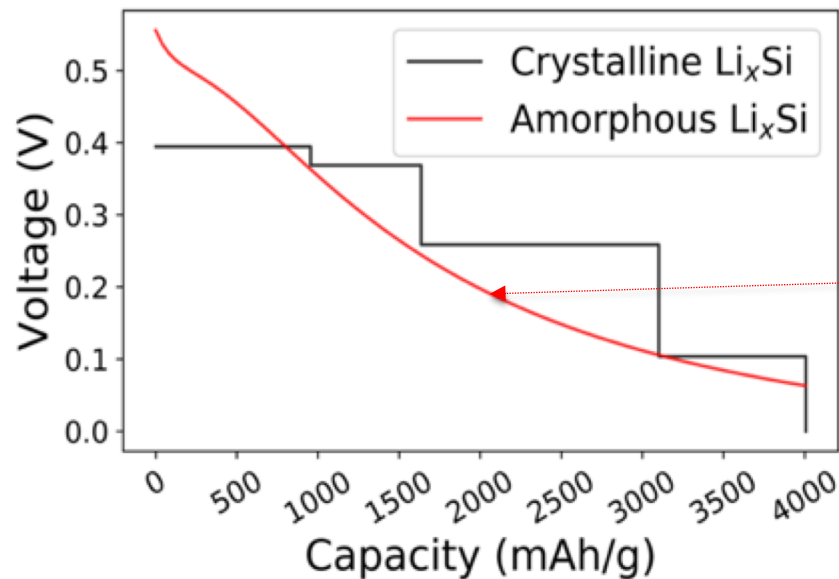


(100) - Si wafer with native SiO<sub>2</sub> surface as working electrode ex-situ  
X-ray Photoelectron Spectroscopy

In agreement with computed predictions; XAS finds that SiO<sub>2</sub> lithiates; exhibiting decreasing Si-O bonds with increasing Li<sub>x</sub>SiO<sub>y</sub> formation as well as Li-O environments at lower voltages; consistent with thermodynamic calculations.

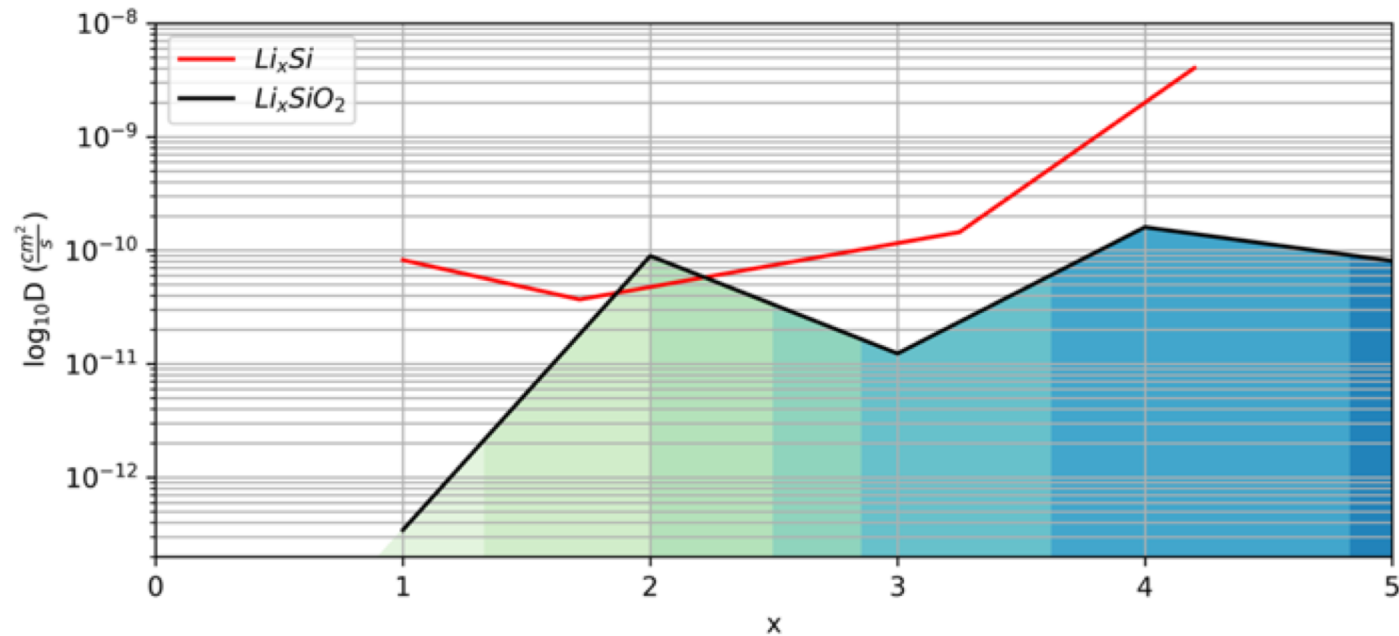
Chuntian Cao, ... Michael Toney, SLAC, in preparation

# Voltage Profiles for $\text{Li}_x\text{Si}$ and $\text{Li}_x\text{SiO}_2$



- The amorphous  $\text{Li}_x\text{Si}$  and  $\text{Li}_x\text{SiO}_2$  phases are found to be metastable as compared to their crystalline and phase separated counterparts; hence amorphization of  $\text{Li}_x\text{Si}$  and  $\text{Li}_x\text{SiO}_2$  is driven by kinetics.
- The voltage profile of amorphous  $\text{SiO}_2$  is 0.8 V higher than that of amorphous Si at low Li contents, providing a clear signature for the lithiation of  $\text{SiO}_2$ .

# Li Self-Diffusivity in amorphous $\text{Li}_x\text{Si}$ and amorphous $\text{Li}_x\text{SiO}_2$



- Li diffusion in amorphous  $\text{Li}_x\text{Si}$  is calculated as  $\sim 10^{-10} \text{ cm}^2/\text{s}$ , and increases beyond  $x = 2$ . This is in agreement in increasing Li-rich environments, promoting fast diffusion, in highly lithiated Si.
- Li self-diffusion in  $\text{Li}_x\text{SiO}_2$  is 2 orders of magnitude lower initially than Si, but rises quickly with Li content and stays around  $10^{-11}$ - $10^{-10} \text{ cm}^2/\text{s}$  after  $x > 2$ .
- Hence, Li diffusion in the native  $\text{SiO}_2$  surface oxide is a kinetic bottleneck for lithiation of Si.



# Conclusions

- In 1 M LiPF<sub>6</sub>/EC, the majority species are solvent-separated ion-pairs (SSIPs); however about 7% contact ion-pairs (CIPs) are also found.
- Adding FEC decreases the solvation strength of the combined solvent, reduces the solvent coordination with Li, causes increase in CIPs, as well as ~10% SSIPs with 1 FEC.
- The significant interaction between oxygen at the SiO<sub>2</sub> interface and Li<sup>+</sup> reduces the CN of EC.
- CIP population is doubled at the interface as compared to the bulk electrolyte
- Higher temperature favors the formation of CIPs as compared to SSIPs, in both bulk and at the interface.
- Majority and interface speciation influences what molecules reduce as a function of voltage such that increased CIP increases PF<sub>6</sub> reduction and even limited FEC coordination with Li decreases its reduction potential
- The amorphous Li<sub>x</sub>Si and Li<sub>x</sub>SiO<sub>2</sub> phases are metastable as compared to their crystalline and phase separated counterparts; hence amorphization of Li<sub>x</sub>Si and Li<sub>x</sub>SiO<sub>2</sub> is driven by kinetics.
- The voltage profile of amorphous SiO<sub>2</sub> is 0.8 V higher than that of amorphous Si at low Li content, providing an electrochemical signature when SiO<sub>2</sub> is lithiated.



# Feedback from Previous Review

Presentation ID	Presentation Title	Principal Investigator (Organization)	Page Number	Approach	Technical Accomplishments	Collaborations	Future Research	Weighted Average
es333	Silicon Electrolyte Interface Stabilization Focus Group†	Anthony Burrell (NREL)	3-293	3.71	3.21	3.64	3.50	3.43

Response to specific reviewer comments are made by team lead Tony Burrell

# Future Work

**We will continue the study of the Si anode and electrolyte interaction (SEI formation) by**

- Exploring the interfacial speciation, spectroscopic characterization, chemical reactions between  $\text{SiO}_2$  and different Si electrolytes, as compared to Si
- Exploring the formation of early SEI components, and their subsequent reactions and products
- Calculating possible alloying components of Si to improve Li diffusion and electrolyte-surface oxide reactivity

# Partners and Collaborations

Alison Dunlop	Dennis Dees	Jinghua Guo	Robert Kostecki
Al-Jassim, Mowafak	Eric Allcorn	John Moseley	Robert Tenent
Andrew Jansen	Fulya Dogan Key	Kaigi Nie	Sang-Don Han
Andrew Norman	Gabriel Veith	Kevin Gallagher	Seoung-Bum Son
Andriy Zakutayev	Ganesan Nagasubramanian	Kevin Wood	Shuo Zhang
Anthony Burrell	Gao Liu	Kevin Zavadil	Stephen Trask
Atetegeb Haregewoin	Glenn Teeter	Kristin Persson	Steve Harvey
Aude Hubaud	Gregory Krumdick	Krzysztof Pupek	Taeho Yoon
Baris Key	Harvey Guthrey	Kyle Fenton	Tingzheng Hou
Brian Cunningham	Ira Bloom	Liang Zhang	Tomonori Saito
Bryant Polzin	Ivana Hasa	Linghong Zhang	Trevor Dzwiniel
Cameron Peebles	Jack Deppe	Lu Zhang	Vincenzo LaSalvia
Christopher Apblett	Jack Vaughey	Lydia Terborg	Wei Tong
Christopher Johnson	Jaclyn Coyle	Matthew Page	Wenquan Lu
Christopher Orendorff	Jagjit Nanda	Min Ling	William Nemeth
Chun Sheng Jiang	James Ciszewski	Nathan Neale	Yangping Sheng
Chunmei Ban	James Gilbert	Niya Sa	Yun Xu
Claus Daniel	Javier Bareno	Pauls Stradins	Zhengcheng Zhang
Daniel Abraham	Jianlin Li	Peter Faguy	Zhijia Du
David Wood	Jing Xu	Phil Ross	

